BIO-INSPIRED CERAMIC/CARBON COMPOSITES

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Mid-project Report

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Introduction

In line with the final objective to fabricate bio-inspired ceramic/CNT or ceramic/carbon composites with nacre-like structures by combining freeze casting with spark plasma sintering our work during this first half of the project has concentrated on the following aspects:

a) Set-up a freeze casting apparatus for the controlled freezing of ceramic suspensions.
b) Structural control of freeze casted materials in particular the lamellae/pore thickness and the structural macroscopic lamellae alignment.
c) Introduction of carbon nanotubes (CNTs) and other C precursors in freeze casted structures.
d) Spark plasma sintering (SPS) of freeze casted structures.
e) Freeze casting of porous silicon carbide materials as a first step in the fabrication of SiC-based composites.

Set-up a freeze casting apparatus

As a part of the project we have built an apparatus for the freeze casting of ceramic suspensions. The apparatus consists of a cold finger immersed in liquid nitrogen with a programmable heater that allows cooling at controlled rates. A Teflon mold containing the ceramic suspensions is placed on the cold finger to promote directional freezing (Fig 1).

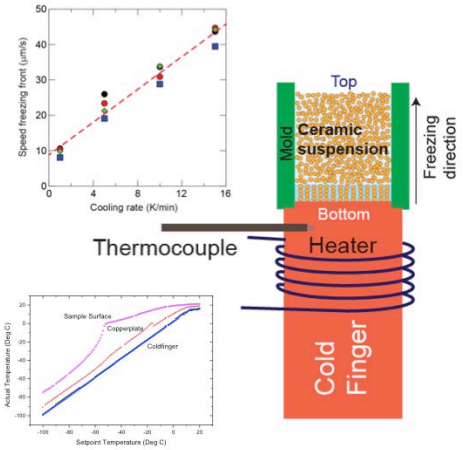

Figure 1. Freeze casting set-up. A teflon mould is filled with a ceramic suspension and placed on a cold finger that can be cooled at controlled rate (between 0 to 15 °C/min) to promote directional freezing. The speeds of the freezing front vary between 10 and 50 µm/s. A set of thermocouples can be used to record the temperature evolution in different locations in the mould and provide basic data needed to model the freeze casting process.

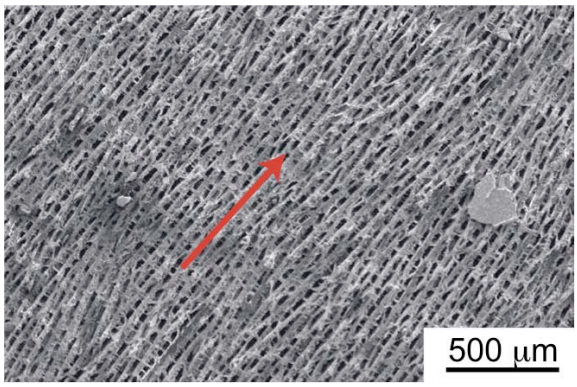

Figure 2. Macroscopic lamellae alingement can be achieved by patterning the cold finger where the ice nucleates.

Control of the lamellar structure

A systematic study was performed to analyze the dependence of the lamellae/pore width of the sintered ceramic scaffolds with the speed of the freezing front and the solid content of the solution. Aluminum oxide suspensions in water with solid contents varying between 20 to 50 wt% were prepared by ball milling for 24 hours, de-aired for 1 hour and placed in the freeze casting apparatus for directional milling. A dispersant (Dolapix, 1.4 wt % to the ceramic powder) and an organic binder (polyvinylalcohol, PVA, 14 wt% to the alumina powder) were added to the suspension. Sucrose (4 wt% of the water) was added to control the structure of the growing ice crystals. Patterning of the cold finger with long microscopic channels has been used to control ice nucleation and growth and achieve macroscopic lamellae alignment over large directions. This strategy will be used to prepare samples with aligned lamellae for subsequent pressing during the preparation of the composite and to control the macroscopic orientation.

Scanning electron micrographs were used to measure the lamellae and pore widths in different places along the sample. In parallel, finite element simulations have been used to visualize the evolution of the temperature gradient in the suspension as the cold finger cools. The structural wavelength (addition of the lamellae and pore widths) decreases with the inverse of the speed of the freezing front (Fig. 2). The results show that this approach can be used to control the wavelength over two decades (from microns to hundred of microns). This tendency has also been observed by other researchers[1, 2] and will allow us to select materials with controlled pore/lamellae sizes.

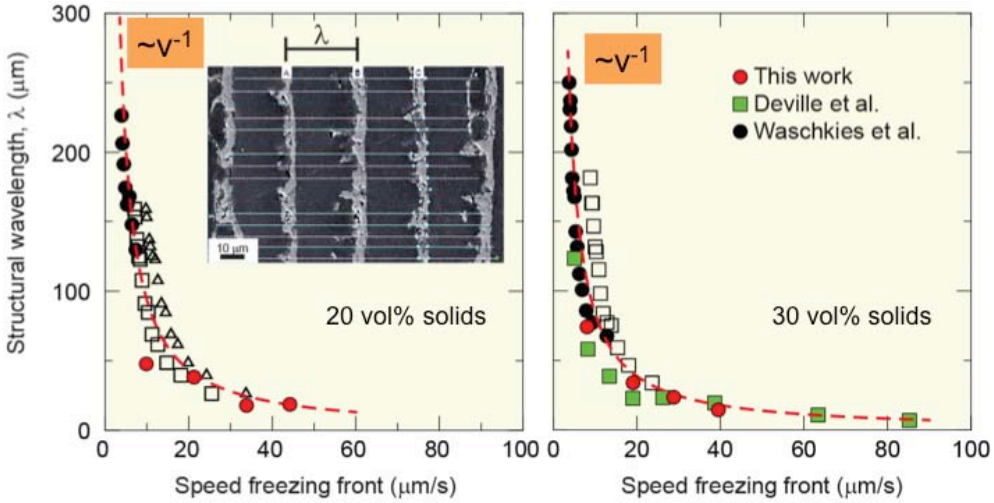

***Figure 2**. Dependence of the structural wavelength (the addition of pore and lamellae width) with ceramic concentration in the suspension and speed of the freezing front. The pore/lamellae widths can be manipulated from microns to hundred of microns. Fast freezing could be used to bring the lamellae width below the micron range[1, 2].*

Introduction of CNTs in freeze casted scaffolds

Two approaches have been used to introduce CNTs in the pores of the freeze casted ceramic scaffolds: “in situ” catalyst mediated growth inside the scaffold and infiltration using nanotube suspensions.

Carbon nanotubes have been grown inside the ceramic scaffold by first infiltrating a solution of Iron (III) Nitrate, $Fe(NO3)_3 \bullet 9H_2O$, in isopropanol (40.4 g in 100 m.) under vacuum into the porous pre-form. The samples are subsequently reduced in $Ar/10\%H_2$ to decorate the internal scaffold surfaces with metallic nanoparticles followed by a growth step in $Ar/H_2/CH_4$. The process is carried out inside a quartz tube furnace at temperatures ranging between 700 to 900 °C and flow rates between 0.0 to 0.5 l/min. During growth the CH_4 can be flowed through water or ethanol to enhance CNT formation.

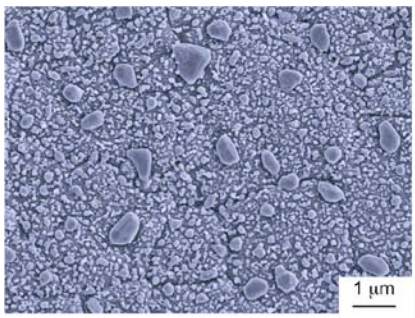

Figure 3. Submicron Fe particles decorate homogeneously the internal surfaces of an Al_2O_3 scaffold fabricated by freeze casting after the infiltration with $Fe(NO3)_3 \cdot 9H_2O$ followed by reduction in $Ar/10\%H_2$ at 800°C.

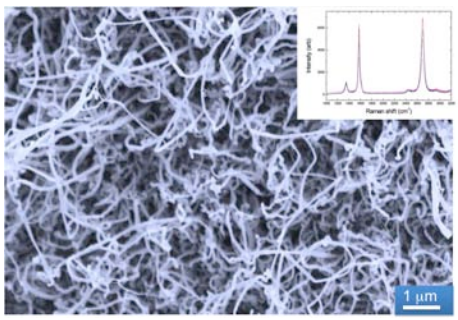

Figure 4. Carbon nanotubes covered homogeneosuly the internal walls of alumina scaffolds (pore size 75 μm) after firing in a 1:1 (volume) mixture of $Ar/10\%H_2$:CH_4. Methane was bubbled through ethanol. The Raman analysis shows the formation of graphitic carbon.

Our results have identified the best temperature range and growth conditions for the homogeneous formation of nanotubes in centimeter-sized scaffolds with pore widths ≥70 µm. Firing at 800 °C in Ar/H_2 results in an homogeneous distribution of submicron Fe particles covering the internal walls of the alumina scaffold (Fig.3). The optimum growth temperature was also 800 °C. Using water as enhancer did not have a positive effect. However, ethanol helped for achieve fully nanotube coverage. Slower gas flow rates (0.2 l/min) also resulted in more homogeneous coverage (Fig. 4).

Aqueous CNT suspensions were prepared by dispersing CVD-grown nanotubes in water. The nanotubes were treated for one hour with HNO_3:H_2SO_4 (3:1) under reflux and subsequently rinsed with de-ionized water. Afterwards they were sonicated in ethanol for 8 hours and dispersed with sodium dodecyl benzenesulfonic acid in water. The resulting dispersion was infiltrated under uniaxial pressure in the porous ceramic scaffold (Fig. 5). Analysis of the sample with scanning electron microscopy shows that the infiltration of large samples was complete and that this is a promising route to introduce nanotubes with controlled length and chemistry inside the porous scaffolds.

As an alternative to nanotubes the scaffolds were infiltrated with solutions of pitch in pyridine (5 g of pitch in 40 ml of pyridine). After infiltration the solvent was removed at 60°C in vacuum. The scaffold was heat treated at 1000 °C for 1 hour in inert (nitrogen) atmosphere to polymerise the pitch. The result was complete infiltration of the pitch across the scaffold.

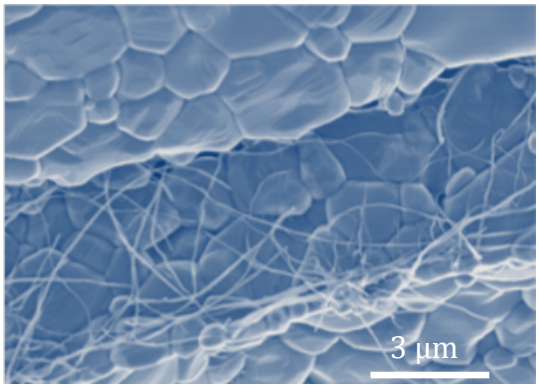

Figure 5. Scanning electron micrograph showing the presence of CNTs in the internal pores of an alumina scaffold after infiltrating a aqueous CNT suspension using uniaxial pressing.

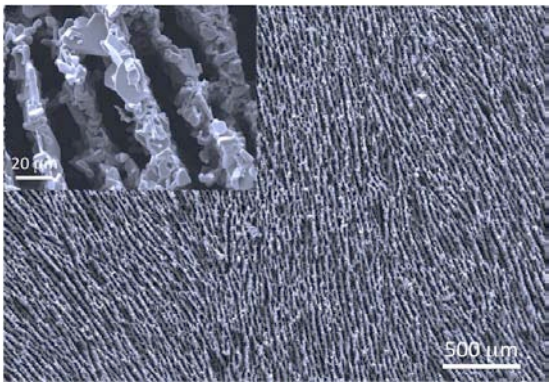

Figure 6. Lamellar SiC carbide scaffold prepared by freeze casting using B as a additive and sintered at 2150 C. Dense lamellae and « in situ » platelet formatin can be observed.

Freeze casting of SiC scaffolds

Silicon Carbide suspensions for freeze casting were prepared by dispersing submicron alpha SiC powders in water (20 vol%) by ball milling for 24 hours followed by de-airing by stirring in vacuum. The suspensions contained PVA and sucrose in the same concentration that for the alumina materials. Two types of suspensions were prepared one using alumina and yittria as sintering additives (6 and 4 wt % respectively) the other with boron (0.35 wt%). After freeze casting (cold finger cooling rate 5 C/min) and sublimating the water by freeze drying, the materials were dried and sintered in Ar in a graphite furnace at temperatures ranging between 1950 and 2150 °C for one hour.

After freeze casting a SiC lamellar structure was obtained in all cases. In the case of silicon carbide with oxide additives the lamellae remain porous after sintering at 1950 °C. Sintering at higher temperatures causes the lost of the layered architecture and results in a porous SiC material. The samples with B retain the layered structure with dense layers after sintering at temperatures up to 2150 °C. The lamellae are dense and the growth of SiC platelets can be observed (Fig. 6).

Spark Plasma Sintering

We have developed an approach for the SPS of the ceramic scaffolds filled with CNTs and carbon precursors. The scaffolds are embedded in ceramic powder and placed inside the SPS die with the lamellae oriented perpendicular to the pressing direction. The densification is followed in situ during SPS to determine optimum temperature and pressure conditions. After pressing at 1500 °C with al force of 10 MPa the SPS samples reach a dense brick-and-mortar architecture with very thin (submicron) C layers separating the ceramic bricks. Raman and xRay diffraction analysis confirm the presence of graphitic carbon both for CNT and pitch infiltrated samples while the nanotubes seem to maintain their structure.

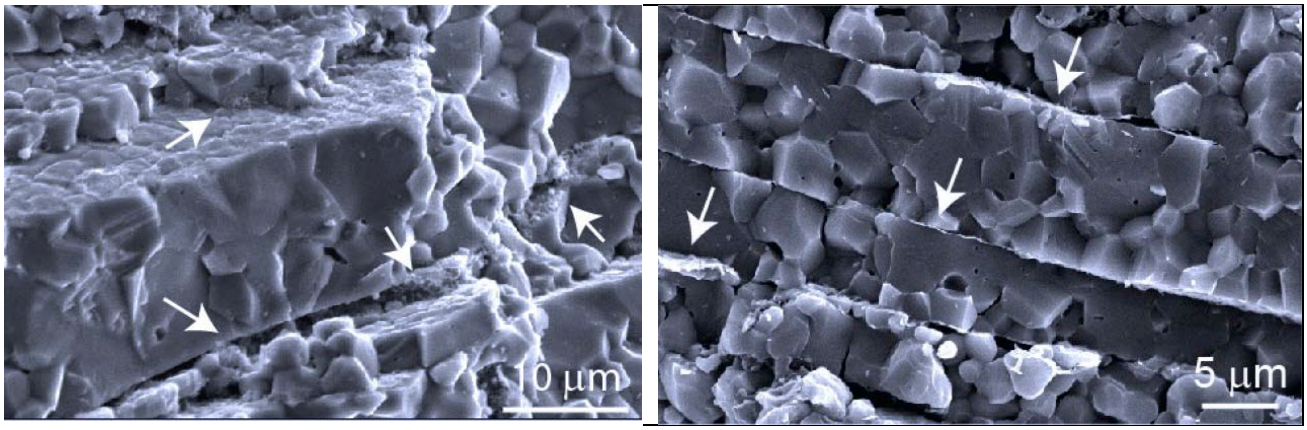

Figure 7. Scanning elelctron micrographs of the fracture surfaces of composite materials obtained after freeze casting alumina scaffolds infiltrated with (a) CNTs and (b) pitch. The composite consists of polycrystalline ceramic bricks separated by thin carbon layers.

Summary

The work performed up to date has shown that is possible to use freeze casting to prepare porous ceramic scaffolds (Al_2O_3 and SiC) with layered structures, lamellae widths in the micron range and microscopic lamellae alignement. We have developed two approaches to introduce CNTs in the scaffolds: in situ growth in the pores or infiltration with nanotube suspensions. In addition these scaffolds could also be infiltrated with other C precursors such as pitch. Spark plasma sintering can be used to compress these infiltrated materials to create brick-and-mortar structures composed of ceramic bricks separated by thin carbon layers.

References

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2. Waschkies, T., R. Oberacker, M.J. Hoffmann, *Investigation of structure formation during freeze-casting from very slow to very fast solidification velocities.* Acta Materialia, 2011. **59**(13): p. 5135-5145.